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Deuteriation and Deuterogenation of Naphthalene and Two Octalins

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Saturation of naphthalene on a Group VIII metal yields *trans*-decalin by *cis* addition of hydrogen to an appropriate octalin intermediate rather than by direct *trans* addition. In like manner, dihydronaphthalene may be an intermediate in the formation of tetralin but with less obvious stereochemical consequences. Treatment of naphthalene and the two stereochemically significant octalins with deuterium gave evidence of a veritable ballet of steps wherein exchange (deuteriation) may be separate from or accompany saturation (deuterogenation). The mechanism of exchange on the aromatic ring or about the double bond seems to be largely "dissociative" with Pt and Ir, partly "associative" with Pd, and in-between with Ru and Rh.

Saturation, accompanied by exchange and double-bond isomerization, and the exchange accompanying the double-bond shift seem to conform to the classical Horiuti-Polanyi associative mechanism. The "dissociative" process is retarded by increased pressure and accelerated by increased temperature. The elusive, but mechanistically important, isomerized olefin that would establish dissociative reversal from the "half-hydrogenated" state has been detected at elevated temperatures on Pd and Rh catalysts. "Release" of intermediates from the surface by desorption may be a matter of degree—complete enough to achieve exchange or isomerization, but not always complete enough for flipover. Diffusion effects cannot be ignored.

Large differences in selectivities of the Group VIII metals may not necessarily reflect differences in mechanisms but rather in relative rates of otherwise identical steps in a complicated sequence.

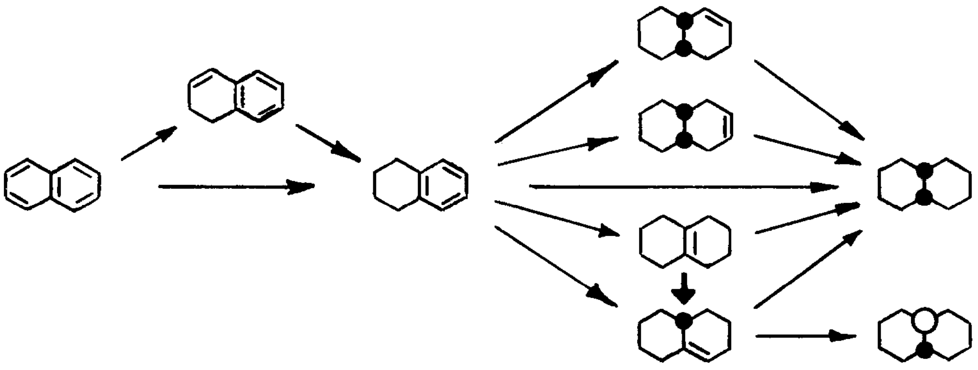
INTRODUCTION

Despite the large commercial potential of naphthalene and its homologs, little is really known about the mechanism of its hydrogenation—a reaction that is perhaps second in importance only to its oxidation. We have studied the stereochemistry of the hydrogenation of the methylnaphthalenes (*1*) and observed that hydrogenation is a more or less stepwise process. We reported the presence of dihydro- and octahydronaphthalenes during the course of saturation, and supported the possibility that they might be intermediates for the formation of *trans* isomers. As part of a program to better understand the stereochemistry of hydrogenation we have deuterogenated naphthalene and the two stereochemically significant octalins, $\Delta^{1,9}$-octalin and $\Delta^{9,10}$-octalin, over five of the Group VIII metals in a range of temperatures and pressures.

Pertinent studies of the exchange and saturation of benzene have been reported (*2*, *3*). The results are generally similar to those we obtained with naphthalene. More recently, Smith and Burwell (*4*) included the octalins in a study of the exchange and saturation of olefins.

The interaction of naphthalene with deuterium is complex. Besides the stepwise addition reactions, there are exchange reactions (deuteriation) that may occur independently of, or in conjunction with, the addition reactions (deuterogenation).

The known steps in hydrogenation can be mapped as follows:



Except for the omission of hexahydronaphthalenes, whose existence may be exceedingly fleeting, this roadmap approximates an early suggestion by Shanfield and Smith (*5*) that hydrogen atoms were added two-by-two during the hydrogenation of 1-methylnaphthalene over a nickel catalyst. The elementary analyses they offered in support may principally reflect mixtures of the methylnaphthalene with the two unresolved tetralins, and mixtures of the latter with the four unresolved methyldecalins; concentrations of dihydro-, hexahydro-, and octahydronaphthalenes were not likely high enough to have been detected without gas chromatography.

The major processes, despite participation of intermediates with partially saturated rings, are (a) saturation of naphthalene to tetralin and (b) saturation of tetralin to *cis*-decalin. These processes can be visualized as occurring during single periods of residence on the catalyst, much as proposed by Balandin (*6*) for monocyclic aromatics and by Linstead (*7*) for phenanthrene. A single period of residence may include more than one adsorption if the rates of adsorption and desorption are comparable with the rates of diffusion to and from the catalyst surface. The predominance of *cis* isomers presupposes the *cis* addition of hydrogen. The *trans* addition mechanism proposed by Gault, Rooney, and Kemball (*8*) seems not to be operative in this system.

From the standpoint of stereochemistry, major interest centers on the octalins as precursors of *trans*-decalin; dihydronaphthalenes may similarly be precursors of *trans*-dimethyltetralins. There is mounting evidence that $\Delta^{1,9}$-octalin is the sole source of *trans*-decalin by the *cis* addition of hydrogen (bottom of roadmap), and that the failure of $\Delta^{9,10}$-octalin to yield only *cis*-decalin arises from prior isomerization to $\Delta^{1,9}$-octalin. Smith and Burwell (*4*) considered $\Delta^{9,10}$-octalin to be the ideal substrate to reveal pure *cis* addition, but in studies of deuterogenation over Adams (PtO_2) catalyst at ambient temperature and 1 atm pressure they observed about equal amounts of *cis*- and *trans*-decalins. From isotopic analyses they concluded that all of the *trans*-decalin and part of the *cis*-decalin had reacted at three or more positions, consistent with prior isomerization of $\Delta^{9,10}$-octalin to $\Delta^{1,9}$-octalin as an integral part of the mechanism.

Some of the complications due to the exchange reactions that seem always to accompany the addition of deuterium to an unsaturated compound are listed in a review by Taylor (*9*):

Redistribution of hydrogen and deuterium in the molecules
Exchange between olefin and deuterium
Exchange between olefin molecules
Double-bond migration
Cis–trans isomerization

TABLE 1

DEUTEROGENATION OF NAPHTHALENE

Experiment	Catalyst	Temp. (°C)	Time (min)	Initial D_2 Press. (psig)	Feed (moles × 10^{-6})			Products (%)				Isotopic dilution of gas (%)
					Naphthalene	Metal	D_2	Decalins	Octalins	Tetralin	Naphthalene	
1	Pt[a]	200	20	500	390	0.6	15 000	—	—	59.0	41.0	0.9
2	Pt	30	90	440	780	5.0	18 300	0.3	—	31.6	68.1	0.06
3	Pt	200	60	370	1560	2.5	15 500	0.5	—	44.0	55.5	4.2
4	Pt	200	165	100	1560	12.5	4 600	—	—	25.7	74.3	38.
5	Ru	25	37	414	1560	5.0	17 200	10.0	1.9[b]	38.5	50.6	0.8
6	Ru	200	2.5	365	1560	5.0	15 800	0.6	0.2	52.5	46.7	0.8
7	Ir	60	70	409	1560	5.0	17 000	7.3	0.3	39.4	53.0	1.3
8	Ir	200	0.5	375	1560	5.0	15 700	4.4	0.4	50.5	44.7	2.6
9	Pd	38	120	417	1560	50.0	17 400	—	—	53.3	46.7	0
10	Pd	200	0.8	390	1560	5.0	16 300	—	—	65.0	35.0	0
11	Pd	200	100	100	1560	25.0	4 600	—	—	41.3	58.7	42
12	Rh	25	10.5	475	1560	5.0	19 700	3.0	0.8	54.4	41.8	0.4
13	Rh	200	2.0	335	1560	5.0	14 100	0.8	0.7	53.3	47.2	0.6
14	Rh	25	30	428	3900	10.0	17 000	4.2	1.2	67.2	27.4	2.1

[a] 0.6% Pt/Al_2O_3, all others were 5% metal on charcoal.

[b] With ruthenium catalyst the octalin fraction was 2/3 $\Delta^{1,9}$-octalin and 1/3 $\Delta^{9,10}$-octalin; with the other catalysts the octalin fraction was chiefly $\Delta^{9,10}$-octalin.

TABLE 2

MASS SPECTROMETRIC ANALYSIS OF DEUTERIATED NAPHTHALENE AND TETRADEUTERONAPHTHALENE

Expt. No.:	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Catalyst:	Pt	Pt	Pt	Pt	Ru	Ru	Ir	Ir	Pd	Pd	Pd	Rh	Rh	Rh
Temp. (°C):	200	30	200	200	25	200	60	200	38	200	200	25	200	25
Press. (psig):	500	440	370	100	414	365	409	375	417	390	100	475	335	428
Naphthalene recovered (%):	41	68	55	74	51	47	53	45	47	35	58	42	47	27
n	Naphtalene Parent Ion, $C_{10}H_{8-n}D_n^+$ (%)													
0	43.9	93.5	28.0	3.00	95.5	89.9	86.8	24.7	99.4	90.0	3.55	87.7	76.8	81.4
1	35.5	5.77	38.2	13.6	3.47	7.06	11.5	36.5	0.54	4.45	14.5	9.5	17.9	13.9
2	15.4	0.53	22.9	27.4	0.72	2.14	1.33	24.8	0.004	4.91	24.5	2.06	3.89	3.63
3	4.17	0.07	8.3	31.5	0.13	0.45	0.20	10.1	0.031	0.27	28.5	0.40	0.89	0.71
4	0.86	0.027	1.95	22.3	0.07	0.22	0.07	2.70	0.004	0.22	18.5	0.19	0.282	0.31
5	0.12	—	0.33	1.59	0.004	0.050	0.005	0.54	0.004	0.022	7.8	0.012	0.062	0.023
6	0.03	0.009	0.043	0.56	0.004	0.031	0.005	0.11	0.004	0.005	2.03	0.009	0.030	0.002
7	0.03	0.013	0.034	0.051	0.018	0.025	0.010	0.12	0.013	0.016	0.34	0.014	0.025	0.006
8	0.12	0.045	0.047	0.009	0.103	0.071	0.088	0.35	0.049	0.055	0.043	0.063	0.035	0.058
D Average	0.84	0.077	1.20	2.65	0.066	0.147	0.159	1.34	0.012	0.17	2.77	0.163	0.305	0.251
	Tetradeuteronaphthalene (Tetralin) Parent Ion, $C_{10}H_{12-n}D_n^+$ (%)													
0	0.1	1.03	0.38	2.71	0.12	0.73	0.04	1.35	0.38	0.12	0.42	0.14	0.28	0.04
1	0.2	0.32	1.19	9.20	0.04	0.22	0.04	6.63	0.11	0.71	2.86	0.11	0.77	0.04
2	0.6	1.32	5.72	17.3	0.54	1.87	0.64	16.9	1.35	4.35	9.5	0.72	5.4	1.52
3	5.6	11.3	18.8	22.2	10.3	16.5	9.7	25.4	15.5	22.1	18.3	10.9	24.5	16.1
4	47.6	77.9	34.9	20.8	81.8	64.3	69.2	24.5	73.6	54.5	23.7	81.0	51.6	73.7
5	30.4	6.0	24.6	15.1	5.1	8.6	15.0	14.5	5.9	14.6	21.4	5.6	10.3	6.7
6	11.6	1.35	10.4	8.2	1.78	3.85	4.1	6.9	3.1	3.24	14.0	1.2	3.75	1.64
7	3.1	0.54	3.07	3.3	0.29	2.09	1.00	2.62	0.38	0.36	6.8	0.26	1.93	0.24
8	0.7	0.25	0.77	0.85	0.083	1.87	0.28	0.94	—	0.040	2.40	0.10	1.05	0.04
9	0.1	—	0.154	0.28	—	0.26	—	0.30	—	—	0.53	—	0.278	—
10	—	—	0.015	—	—	0.25	—	0.11	—	—	0.11	—	0.085	—
11	—	—	—	—	—	0.08	—	—	—	—	—	—	—	—
12	—	—	—	—	—	0.06	—	—	—	—	—	—	—	—
D Average	4.58	3.92	4.23	3.51	3.98	4.14	4.16	3.58	3.95	3.89	4.34	3.95	3.91	3.92

	Fragment Ion Formed by Loss of Ethylene from Tetralin, $C_8H_{8-n}D_n^+$ (%)													
0	2.9	1.34	2.2	7.0	0.42	0.52	0.44	7.35	0.88	1.52	3.09	0.31	1.55	0.46
1	8.9	7.2	13.9	20.7	6.5	9.86	6.6	25.1	2.36	14.4	13.3	6.7	15.6	9.52
2	49.5	68.7	40.3	28.6	70.9	60.9	64.9	34.3	73.9	57.1	26.0	71.1	55.9	67.7
3	28.1	18.8	29.8	24.2	19.6	20.4	23.1	21.3	19.8	22.4	28.1	19.6	19.8	19.5
4	8.4	2.66	11.0	13.2	2.23	5.4	4.2	8.4	2.80	4.11	18.8	2.06	5.1	2.46
5	1.8	1.23	2.55	4.86	0.40	1.76	0.66	2.61	0.20	0.45	8.1	0.24	1.32	0.33
6	0.3	0.16	0.38	1.22	0.022	0.86	0.13	0.75	0.012	0.089	2.24	0.06	0.50	0.043
7	0.1	0.022	0.024	0.15	—	0.167	—	0.14	—	—	0.35	—	0.180	—
8	—	—	—	0.046	—	0.147	—	0.028	—	—	0.002	—	0.050	—
D Average	2.37	2.19	2.43	2.36	2.18	2.31	2.27	2.10	2.22	2.15	2.81	2.17	2.19	2.15
% D lost with ethylene fragment	48	44	43	33	45	44	45	41	44	45	35	45	44	45

Self-hydrogenation and decomposition
Dehydrogenation and polymerization

This list is no doubt incomplete. However, *cis–trans* isomerization would not apply in the cyclic olefins because of ring constraint. Such reactions as decomposition and polymerization may not be significant since our experiments were stopped at partial conversion. However, one obvious result of exchange that must be considered is the release of hydrogen to the catalyst, where it may either exchange with gas-phase deuterium or remain on the surface to dilute the adsorbed deuterium and compete with it in subsequent exchange or addition. In either case the reactants would see a mixture of hydrogen and deuterium.

Isotopic analyses of the products will show the distribution of species containing a given number of deuterium atoms. What is needed for elucidation of mechanism is the distribution of species that have reacted with a given number of deuterium plus hydrogen atoms. These can be computed (*4*) provided certain conditions apply. If none of the hydrogen is desorbed to the gas phase, a constant D/H ratio will be established on the catalyst. Even if some of the hydrogen is desorbed, isotopic dilution of the gas phase will not be serious if a large excess of deuterium is used.

EXPERIMENTAL

Materials. Naphthalene of high purity was obtained from a petroleum reformate. Octalins were prepared by reducing pure naphthalene with lithium metal in refluxing ethylamine. The main products were $\Delta^{9,10}$-octalin and $\Delta^{1,9}$-octalin in about 4:1 ratio, along with traces of *trans*-$\Delta^{1,2}$-octalin and *trans*-$\Delta^{2,3}$-octalin. The $\Delta^{1,9}$-octalin was separated by preparative-scale gas chromatography on an efficient Carbowax column. The $\Delta^{9,10}$-octalin was readily purified by selective hydrogenation of all other isomers over an iridium catalyst [platinum may also be used (*4*)]; it was separated from the resulting decalins with silica gel. The $\Delta^{1,9}$-octalin was about 99% and the $\Delta^{9,10}$-octalin about 99.5% pure; the contaminant in each case being the other isomer.

Catalysts consisting of 5% ruthenium, rhodium, palladium, iridium, or platinum on charcoal were purchased from Engelhard Industries. A commercial reforming catalyst consisting of 0.6% platinum on alumina was used in a few experiments.

Apparatus. Deuterogenations were done in small stirred batch reactors. In elevated-temperature experiments, rapid heating was obtained by dipping the vessel in a constant-temperature oil bath.

Methods. The catalysts were used without pretreatment. The sample of naphthalene or octalin, usually 50-200 mg, was dissolved in 1 ml of cyclohexane, and in the case of the octalins the solution was filtered through a ¼-inch layer of silica gel in the tip of a medicine dropper directly into the reaction vessel to remove catalyst poisons. Experiments were terminated after a predetermined pressure drop. The product was analyzed by gas chromatography on a Carbowax column. Tetralin and the recovered naphthalene were separated by gas chromatography for isotopic analysis by low-voltage mass spectrometry (*10*). The measurements were made on a Consolidated Model 21-103 instrument. Besides the usual count of deuterium atoms, some knowledge of their locations was gained from the fragmentation of tetralin at the lowest effective voltage.

RESULTS

Naphthalene. Experimental conditions for the deuterogenation of naphthalene, as well as composition of feed and products, are in Table 1. The data permit comparison of five of the Group VIII metals at two widely separated temperatures. Comparisons can also be made of platinum on two different supports, and of platinum and palladium at lower pressures. Isotopic analyses of the recovered naphthalene and of the parent and parentless ethylene ions of tetralin are in Table 2. Estimates of isotopic dilution of the gas phase are included.

Octalins. Similar data for the octalins are in Table 3. Isotopic analyses for the

TABLE 3
Deuterogenation of Octalins

Experiment	Catalyst	Temp. (°C)	Time (min)	Feed (moles × 10^{-6})			Products (%)			
							Octalins		Decalins	
				Metal	Octalin	D_2	$\Delta^{1,9}$	$\Delta^{9,10}$	*cis*	*trans*
Feed: $\Delta^{1,9}$-octalin										
15	Pt[a]	100	30	2.5	660	15 000	51.2	2.6	19.9	26.3
16	Pt[a]	200	10	6.3	660	15 000	0.1	4.4	34.3	61.2
17	Pt	25	0.75	1.3	600	10 800	1.5	1.0	37.0	60.5
18	Ru	25	37	50	530	12 000	37.7	0.9	45.6	15.8
19	Ir	25	3	6.5	330	12 000	24.9	0.7	55.0	19.4
20	Pd	25	1	4.7	530	11 000	38.3	7.7	11.3	52.7
21	Rh	25	0.25	2.4	530	11 000	34.5	1.5	37.6	26.4
Feed: $\Delta^{9,10}$-octalin										
22	Pt[a]	200	40	2.5	660	15 000	—	16.7	38.7	44.6
23	Pt	25	4	1.3	660	10 800	—	63.2	24.5	12.3
24	Ru	25	63	25	660	12 000	—	31.5	64.9	3.6
25	Ir	25	23	26	1320	11 000	—	55.1	43.9	1.0
26	Pd	25	1.3	23	660	12 000	0.3	48.3	8.0	43.4
27	Rh	25	1.5	24	660	12 000	—	26.7	62.2	11.1

[a] The catalyst for the high-temperature experiments was 0.6% Pt/Al_2O_3; all others were 5% metal on charcoal.

products from the ambient-temperature experiments are in Tables 4 and 5. Isotopic analyses for the products from experiments with platinum catalysts (Experiments 15, 16, 17, 22, and 23) are included in Tables 6 and 7 along with data from the atmospheric-pressure experiments of Smith and Burwell (*4*).

Discussion

Operative reactions during the catalytic deuterogenation of naphthalene and of the octalins included exchange and saturation and, to a lesser degree, dehydrogenation and double-bond isomerization. Experiments with a variety of transition metal catalysts over a range of conditions suggest that several mechanisms may operate simultaneously. One of the major questions is whether the initial process is "associative" (*3*) or "dissociative" (*11*). Bits of evidence from our experiments will be cited in support of one or another viewpoint.

Under the relatively high pressures of our experiments, saturation is favored relative to exchange. Comparatively large yields (as much as 90+%) of tetralin-$(h,d)_4$ and decalin-$(h,d)_2$ species from saturation of naphthalene and octalin, respectively, argue that the initial process for saturation is "associative."

Exchange may precede, accompany, or follow saturation of naphthalene to tetralin; similarly for the octalins exchange may precede or accompany saturation, but the fully saturated decalins were not further exchanged. The exchange process on the octalins seems to be by a "dissociative" mechanism. It is rather difficult to believe that the double bond of $\Delta^{1,9}$-octalin could have been disrupted by half-hydrogenation, as in an associative process, and yet have been left intact in its original position despite the fact that unsaturation in the 9,10-position is thermodynamically favored about 12 to 1.

Exchange on benzene was considered by Kemball (*12*) to resemble exchange on saturated hydrocarbons, i.e., the resonance stability of the ring would not be destroyed and the initial step would be a dissociative adsorption. Mono-exchange would occur through a series of phenyl radicals. Multiexchange could occur by conversion of some

TABLE 4

ISOTOPIC ANALYSIS OF $\Delta^{1,9}$-OCTALIN DEUTEROGENATION PRODUCTS

Expt. No.:	17			18			19			20				21			
Catalyst:	Pt			Ru			Ir			Pd				Rh			
Yield (%):	1.5	37.0	60.5	37.7	45.6	15.8	24.9	55.0	19.4	7.7	38.3	11.3	52.7	1.5	34.5	37.6	26.4
		Decalin			Decalin			Decalin		Octalin		Decalin		Octalin		Decalin	
n	$\Delta^{1,9}$-octalin	*cis*	*trans*	$\Delta^{1,9}$-octalin	*cis*	*trans*	$\Delta^{1,9}$-octalin	*cis*	*trans*	$\Delta^{9,10}$	$\Delta^{1,9}$	*cis*	*trans*	$\Delta^{9,10}$	$\Delta^{1,9}$	*cis*	*trans*
0	93	0.8	1.0	92.7	4.1	3.9	96.6	1.6	2.7	13.7	72.2	2.2	2.8	36	92.9	3.5	4.2
1	4	9.0	10.8	5.7	16.3	16.1	2.7	10.3	10.7	51.9	21.9	11.3	12.9	25	4.9	16.8	17.6
2	1	77.4	80.4	0.7	44.8	42.2	0.4	46.5	41.2	24.8	4.5	38.2	39.6	23	1.4	35.3	35.5
3	1	9.9	6.2	0.6	21.8	23.1	0.2	25.7	27.3	6.5	0.8	27.4	27.0	9	0.6	23.0	24.9
4	1	2.0	1.3	0.2	7.8	11.0	0.1	8.8	13.3	2.2	0.4	12.4	11.2	4	0.1	10.7	12.3
5	—	0.6	0.3	0.1	3.4	2.9	—	3.8	3.2	0.5	0.1	5.1	4.3	1	0.1	5.8	4.1
6	—	0.2	—	—	1.0	0.7	—	1.9	1.2	0.2	0.1	2.0	1.4	1	—	2.5	1.2
7	—	0.1	—	—	0.5	0.1	—	0.9	0.4	0.2	—	0.6	0.7	1	—	1.1	0.2
8	—	—	—	—	0.1	—	—	0.4	—	—	—	0.3	0.1	—	—	0.6	—
9	—	—	—	—	0.1	—	—	0.1	—	—	—	0.1	—	—	—	0.5	—
10	—	—	—	—	0.1	—	—	—	—	—	—	0.2	—	—	—	0.1	—
11	—	—	—	—	—	—	—	—	—	—	—	0.1	—	—	—	0.1	—
12	—	—	—	—	—	—	—	—	—	—	—	0.1	—	—	—	—	—
Av. No. D Atoms	0.13	2.06	1.97	0.10	2.32	2.33	0.05	2.57	2.55	1.35	0.36	2.69	2.54	1.3	0.10	2.62	2.42

TABLE 5

Isotopic Analysis of $\Delta^{9,10}$-Octalin Deuterogenation Products

Expt. No.: Catalyst:	23 Pt			24 Ru			25 Ir			26 Pd			27 Rh		
Yield (%):	63.2	24.5	12.3	31.5	64.9	3.6	55.1	43.9	1.0	48.3	8.0	43.4	26.7	62.2	11.1
		Decalin			Decalin			Decalin			Decalin			Decalin	
n	$\Delta^{9,10}$-octalin	*cis*	*trans*	$\Delta^{9,10}$-octalin	*cis*	*trans*	$\Delta^{9,10}$-octalin	*cis*	*trans*[a]	$\Delta^{9,10}$-octalin	*cis*	*trans*	$\Delta^{9,10}$-octalin	*cis*	*trans*
0	98.8	0.8	1.1	91.1	7.7	7.6	88.8	1.4	1	90.7	5.5	4.0	69.5	2.3	4.0
1	0.8	4.9	3.3	5.1	18.9	14.8	5.4	5.8	2	6.1	7.2	8.3	16.9	5.4	7.6
2	0.2	36.7	17.1	1.7	24.5	21.6	3.3	19.1	22	2.1	17.8	16.2	6.4	10.8	13.0
3	0.1	40.1	67.9	0.8	19.2	20.7	1.3	26.8	24	0.6	22.6	34.2	3.1	16.1	19.2
4	0.1	13.1	8.7	0.5	13.1	15.2	1.0	20.1	22	0.4	21.8	20.5	2.0	17.9	18.1
5	—	2.7	1.4	0.4	7.8	9.6	0.1	11.4	13	0.1	13.4	10.1	1.0	16.1	15.0
6	—	1.1	0.5	0.2	4.4	5.3	0.1	7.7	10	—	7.2	4.4	0.5	14.2	9.4
7	—	0.3	—	0.1	2.4	3.2	—	3.7	3	—	3.0	1.6	0.4	7.6	5.6
8	—	0.1	—	0.1	1.2	2.0	—	2.0	2	—	1.2	0.7	0.2	4.2	3.4
9	—	0.1	—	—	0.5	—	—	1.1	1	—	0.3	—	—	2.9	2.2
10	—	0.1	—	—	0.2	—	—	0.8	—	—	—	—	—	2.0	1.7
11	—	—	—	—	0.1	—	—	0.1	—	—	—	—	—	0.4	0.7
12	—	—	—	—	—	—	—	—	—	—	—	—	—	0.1	0.1
Av. No. D Atoms	0.02	2.76	2.86	0.16	2.77	2.99	0.21	3.69	3.8	0.14	3.41	3.19	0.59	4.51	4.07

[a] The *trans*-decalin sample from Ir was too small for precise analysis.

TABLE 6

ISOTOPIC ANALYSIS OF $\Delta^{1,9}$-OCTALIN[a] DEUTEROGENATION PRODUCTS. PLATINUM CATALYSTS—VARIOUS CONDITIONS

Expt. No.:	30(4)			17			15			16			
Catalyst:	PtO_2 (Adams)			5% Pt/C			0.6% Pt/Al_2O_3			0.6% Pt/Al_2O_3			
Temp. (°C):	25			25			100			200			
Press. (Atm):	1			25			34			34			
Yield (%):	63.4	19.8	16.8	1.5	37.0	60.5	51.2	19.9	26.3	0.1	4.4	34.3	61.2
		Decalin			Decalin			Decalin				Decalin	
n	$\Delta^{1,9}$-octalin	*cis*	*trans*	$\Delta^{1,9}$-octalin	*cis*	*trans*	$\Delta^{1,9}$-octalin	*cis*	*trans*	$\Delta^{1,9}$-octalin	$\Delta^{9,10}$-octalin	*cis*	*trans*
0	96.3	4.1	4.1	93	0.8	1.0	95.4	4.8	5.6		15.1	0.5	0.4
1	3.1	22.1	26.9	4	9.0	10.8	3.1	10.6	11.0		30.1	5.9	6.3
2	0.29	52.2	56.0	1	77.4	80.4	0.7	71.4	73.2		24.2	41.1	45.2
3	0.09	14.5	9.5	1	9.9	6.2	0.2	10.3	8.5		12.8	24.2	23.1
4	0.11	4.9	2.4	1	2.0	1.3	0.6	1.9	1.5		8.2	12.0	12.4
5	0.05	1.4	0.68	—	0.6	0.3	—	1.0	0.2		4.6	7.2	6.3
6	0.02	0.50	0.24	—	0.2	—	—	—	—		2.3	4.1	3.2
7	0.005	0.17	0.08	—	0.1	—	—	—	—		1.4	2.5	1.7
8	—	0.07	0.03	—	—	—	—	—	—		0.7	1.3	0.8
9	—	0.029	0.01	—	—	—	—	—	—		0.4	0.9	0.2
10	—	0.015	0.002	—	—	—	—	—	—		0.2	0.3	0.4
11	—	0.005	—	—	—	—	—	—	—		—	—	—
12	—	0.004	—	—	—	—	—	—	—		—	—	—
Av. No. D Atoms	0.048	2.02	1.83	0.13	2.06	1.97	0.075	1.98	1.90		2.12	3.10	2.90

[a] $\Delta^{9,10}$-octalin was present as an impurity in the $\Delta^{1,9}$-octalin feed to the extent of 1% in Experiment 17 and 1.7% in Experiment 15 and Experiment 16; it was present in the products to the extent of 1.0% in Experiment 17 and 2.6% in Experiment 15 but was recovered for analysis only in Experiment 16.

TABLE 7

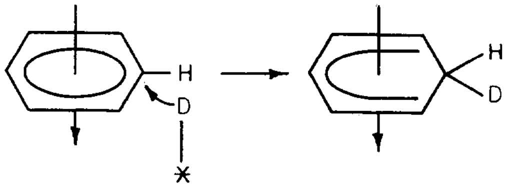
Isotopic Analysis of $\Delta^{9,10}$-Octalin Deuterogenation Products. Platinum Catalysts—Various Conditions

Expt. No.:	25(4)			27(4)			23			22		
Catalyst:	PtO_2 (Adams)			PtO_2 (Adams)			5% Pt/C			0.6% Pt/Al_2O_3		
Temp. (°C):	25			25			25			200		
Press. (Atm):	1			1			25			34		
Yield (%):	18.8	37.4	43.8	44.7	33.7	21.6	63.2	24.5	12.3	16.7	38.7	44.6
		Decalin			Decalin			Decalin			Decalin	
n	$\Delta^{9,10}$-octalin	*cis*	*trans*	$\Delta^{9,10}$-octalin	*cis*	*trans*	$\Delta^{9,10}$-octalin	*cis*	*trans*	$\Delta^{9,10}$-octalin	*cis*	*trans*
0	81.2	7.9	6.0	88.4	2.9	2.2	98.8	0.8	1.1	46.4	0.3	0.2
1	11.2	11.9	11.7	7.6	10.0	8.4	0.8	4.9	3.3	23.2	1.5	0.4
2	3.6	29.6	30.8	2.3	31.1	28.6	0.2	36.7	17.1	13.3	10.1	6.4
3	1.9	29.9	35.2	0.85	32.3	40.5	0.1	40.1	67.9	6.8	24.3	28.6
4	1.3	11.4	9.3	0.51	13.9	12.2	0.1	13.1	8.7	4.4	22.9	24.2
5	0.51	4.4	3.5	0.21	4.9	4.2	—	2.7	1.4	2.7	15.1	16.4
6	0.19	2.4	1.8	0.09	2.4	2.0	—	1.1	0.5	1.6	10.9	10.2
7	0.06	1.3	0.91	0.03	1.2	1.0	—	0.3	—	0.8	6.6	6.4
8	0.02	0.67	0.42	0.01	0.65	0.50	—	0.1	—	0.3	3.7	3.4
9	0.01	0.30	0.18	0.003	0.36	0.26	—	0.1	—	0.3	2.3	2.2
10	0.002	0.13	0.08	—	0.20	0.13	—	0.1	—	0.2	1.0	1.0
11	—	0.05	0.03	—	0.11	0.07	—	—	—	—	0.5	0.2
12	—	0.04	0.03	—	0.05	0.04	—	—	—	—	0.3	0.4
13	—	0.01	0.01	—	0.03	0.02	—	—	—	—	0.2	—
14	—	0.02	0.01	—	0.01	0.02	—	—	—	—	0.3	—
15	—	0.005	0.003	—	0.005	0.003	—	—	—	—	—	—
Av. No. D Atoms	0.337	2.63	2.58	0.186	2.85	2.85	0.02	2.76	2.86	1.24	4.50	4.48

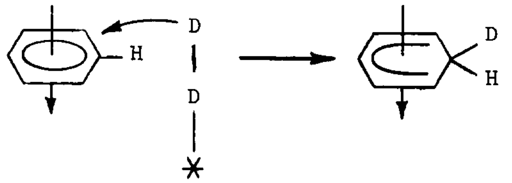
of the phenyl radicals to phenylene biradicals, etc.

Experiments on metal catalysts showed that the initial product was largely monodeuterobenzene. The presence of more highly exchanged species as initial products indicated the concurrent operation of a multi-exchange process. A third process gave small amounts of perdeuterobenzene. However, the per-exchange process was more pronounced on saturated hydrocarbons. Thus cyclohexane yielded more perdeuterocyclohexane, and for *n*-hexane on a palladium film, Meyer and Kemball (*13*) reported more than 80% initial perdeutero-*n*-hexane.

Although Anderson and Kemball (*2*) originally favored the dissociative mechanism, more recently Harper and Kemball (*14*) have questioned it. Burwell and Loner (*15*) and Siegel (*16*) favor the dissociative picture and find it difficult to rationalize associative adsorption if topside removal of hydrogen must follow the underside addition of deuterium.



Gault, Rooney, and Kemball (*8*) see evidence for the topside addition to a flatwise adsorbed (pi-bonded) benzene molecule from an adsorbed but undissociated deuterium molecule. Hartog, Tebben, and Weterings (*17*) support this view.



Our data do not seem to support topside addition. In fact, the total absence of *trans*-decalin-$(h,d)_2$ in the *trans*-decalin obtained in the deuterogenation of $\Delta^{9,10}$-octalin (Experiments 23 and 26) shows clearly that topside addition could not have been operative under our conditions. Either saturation and exchange take place by different mechanisms, or a rationalization of the topside removal of hydrogen must be found.

Exchange on Naphthalene

In some of the experiments (Table 2) isotopic distributions of the recovered naphthalene showed evidence of the same kind of mono-exchange, multi-exchange, and per-exchange processes that were operative on benzene (*2*). These we consider to be dissociative processes. Some of the apparent multi- and per-exchange may result from a sequence of mono- exchange events during diffusion from a catalyst pore. The heterogeneous catalytic reactor in which all molecules experience the same contact time has not yet been devised. Other kinds of reactions were evident in other experiments. For example, palladium at high temperature showed evidence of two-by-two exchange, and platinum at high temperature and low pressure showed a large discontinuity after four exchanges, as if it was incapable of propagating exchange past the bridgeheads. These may be associative processes. Both mechanisms may be more or less operative on all catalysts.

Dissociative mechanisms. The mono-exchange process predominated with platinum, iridium, and palladium catalysts at 200° and high pressure (Experiments 1, 3, 8, and 11). A detailed analysis of the results with one of the platinum catalysts (Experiment 1) is given in Table 8. The first column records the isotopic analysis from mass spectrometry. The small upturn at d_8 reflects a very minor but real contribution from a per-exchange mechanism. As a result of exchange some hydrogen (about 3%) became mixed with the deuterium on the catalyst. Per-exchange gave a random distribution of (h_{8-n}, d_n) species. Relative concentrations, as calculated from the expansion of $(h+d)^8$ for $h = 0.03$* and $d = 0.97$, and listed in the second column, are consistent with the observed yields of naphthalene-d_7 and d_8. The remaining terms in the observed distribution were similarly corrected for incorporation of hydrogen by mechanisms other than per-exchange on the basis that each observed isotopic species contained a random distribution of (h,d) species. The computed naphthalene-$(h,d)_n$ distribution is given in the third column. If the reaction is indeed a sequence of independent mono-exchange steps, the kinetic distribution will be the same as an equilibrium or random distribution for a mixture of isotopic species with the same mean deuterium content (*12*). Such a distribution, calculated from the expansion of $(h+d)^8$ for $h = 0.893$ and $d = 0.107$, corresponding to 0.856 exchanged positions, is given in the last column. The random distribution falls off too rapidly, as if multi-exchange was operative to some degree.

TABLE 8

CALCULATED $(h,d)_n$ VALUES AND D/H RATIO FOR NAPHTHALENE. (D/H = 32.3)

n	Obs d_n	Calculated (h_{8-n},d_n)	Calculated $(h,d)_n$	Random $(h,d)_n$[a]
0	43.9	—	42.84	40.4
1	35.5	—	35.61	38.8
2	15.4	—	15.98	16.27
3	4.17	—	4.45	3.90
4	0.86	—	0.95	0.58
5	0.12	—	0.13	0.056
6	0.03	0.003	0.04	0.0034
7	0.03	0.029	0.00	0.0001
8	0.12	0.12	0.00	0.000
D Av.	0.84	(H,D)	0.856	0.856

[a] Random distribution computed for 0.856 exchanged positions.

A more convenient way to examine whether the experimental isotopic distributions conform with the sequential mono-exchange model is to compute constants (corresponding to random distribution) for the stepwise process:

$$d_0 \rightarrow d_1 \rightarrow d_2 \rightarrow d_3 \rightarrow d_4 \rightarrow d_5 \rightarrow d_6 \rightarrow d_7 \rightarrow d_8$$

and compare them with the corresponding "kinetic" constants listed in Table 9. Thus $K_1 = (d_1)^2/(d_0)(d_2)$ and in general $K_i = (d_i)^2/(d_{i-1})(d_{i+1})$. Numerical values of the K_i's for an eight step process are calculated directly from appropriate terms of the binomial expansion of $(x+y)^8$. Thus: $K_1 = (8x^7y)^2/(x^8)(28x^6y^2) = 2.29$; $K_2 = 1.75$; $K_3 = 1.60$; $K_4 = 1.56$; $K_5 = 1.60$; $K_6 = 1.75$; $K_7 = 2.29$.

Reference to Table 9 shows that Experiments 1, 3, 8, and 11 gave the most nearly random distributions. All were at high temperature (200°) but with three different metals—platinum, iridium, and palladium. In each case the observed constants fall below the theoretical, showing that some multi-exchange always accompanied the predominant mono-exchange. Experiments 2, 5, 7, 9, and 13 gave small constants with no evident pattern, as if the mechanism was predominantly multi-exchange. All except Experiment 13 were at low temperature, and exchange was much slower than saturation.

Associative mechanisms. Palladium (Experiment 10, Table 9) gave a strong indication of two-by-two exchange, i.e., K_2 and K_4 were large. Palladium is unique in its ability to adsorb olefins in the presence of aromatics. The preferential formation of naphthalene-d_2 is rationalized in terms of partial saturation of the "diolefinic" ring of naphthalene to a dihydronaphthalene-d_2 that could desorb, flip over, and be dehydrogenated from the other side (see scheme, p. 445). Repetition of the same process could account for the enhanced yield of naphthalene-d_4. Actually, the major process under high deuterium pressure (Experiment 10), was not exchange but saturation to teralin-d_4. With no more "olefin" for palladium to attack, the reaction stopped cleanly at the tetralin stage. By the way of contrast, low pressure (Experiment 11) reduced the rate of saturation to tetralin, thereby providing time for extensive dissociative adsorption

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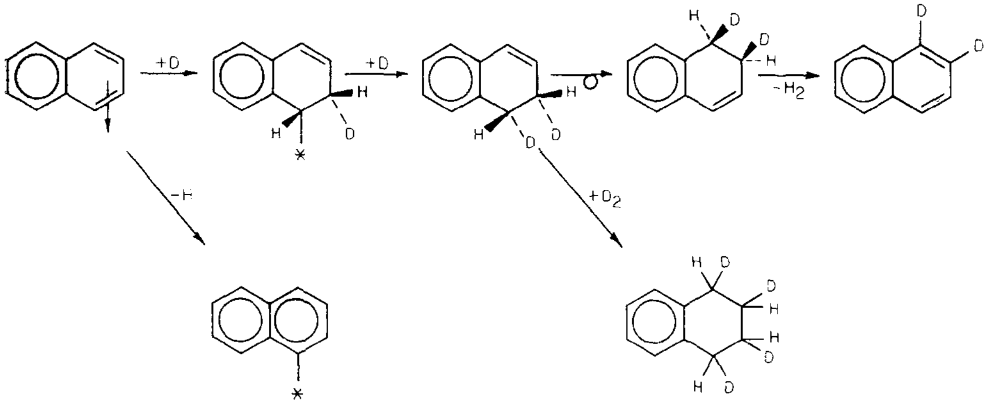
* The surface D/H ratio used here was selected by trial and error (see Table 10) to account for the deuterium-deficient tetralins, principally tetralin-d_3.

TABLE 9

COMPARISON OF "KINETIC" CONSTANTS FOR EXCHANGE ON NAPHTHALENE WITH THEORETICAL EQUILIBRIUM CONSTANTS, K_i

Expt. No.: i	K_i	1	3	11	8	13	7	9	2	5	4	6	14	12	10
1	2.29	1.86	2.26	2.40	2.17	1.07	1.15	0.73	0.67	0.18	2.25	0.26	0.65	0.5	0.05
2	1.75	1.60	1.65	1.45	1.66	0.95	0.77	—	0.70	0.35	1.75	1.43	1.33	1.12	15.0
3	1.60	1.31	1.54	1.79	1.52	0.72	0.43	—	0.34	0.95	1.62	0.43	0.45	0.41	0.07
4	1.56	1.48	1.39	1.54	1.33	1.43	—	—	—	—	10.0	2.15	2.9	7.5	37.0
5	1.60	—	1.30	1.62	1.30	—	—	—	—	—	0.20	—	—	—	—
6	1.75	—	—	1.55	—	—	—	—	—	—	3.9	—	—	—	—
7	2.29	—	—	1.32	—	—	—	—	—	—	0.52	—	—	—	—



and the resulting sequence of mono-exchange steps. Two-by-two exchange shows up to a smaller extent with ruthenium and rhodium catalysts (Experiments 6, 12, and 14); a stepwise exchange process is also evident but we could not distinguish whether it is predominantly mono-exchange or predominantly multi-exchange.

Platinum at low pressure (Experiment 4) gave a peculiar result. The first four exchanges fit the random distribution pattern, perhaps fortuitously. A distinct discontinuity occurred between d_4 and d_5, as if only one ring was involved and the exchange process could not propagate past the bridgeheads. This suggests associative adsorption to give a species corresponding to a half-hydrogenated diolefin. If so, exchange could propagate around four carbons of the nonaromatic ring, and eventually, because of the low pressure, some would desorb as exchanged naphthalene rather than being saturated to the tetralin.

Saturation of Naphthalene to Tetralin

The metals differed in the selectivities with which they saturated naphthalene to tetralin (Table 1). The selectivities were in the order $\mathrm{Pd} > \mathrm{Pt} > \mathrm{Rh} > \mathrm{Ir} > \mathrm{Ru}$. The unique ability of palladium to stop at the tetralin stage is in keeping with its ability to saturate olefins in the presence of aromatics and supports the notion that naphthalene may be adsorbed as if it was a cyclic diolefin fused to an aromatic ring.

Cyclic olefins are present in higher concentrations during the hydrogenation of naphthalene (*1*) than has been observed with monocylic aromatics (*18, 19*). Rhodium gives the highest concentration of octalins, $\Delta^{9,10}$-octalin being the major isomer. With ruthenium catalyst, $\Delta^{1,9}$-octalin predominates initially.

In the products of deuterogenation, the major isotopic species of tetralin generally contained four atoms of deuterium. The question of whether exchange accompanies saturation is clouded by exchange that preceded saturation. Anderson and Kemball (*2*) felt that the saturation of benzene was not accompanied by exchange, but Harper and Kemball (*14*) found extensive exchange of ring hydrogens during the saturation of *p*-xylene.

Corrections can be made for the reuse of hydrogen that is returned to the catalyst by all exchange processes (before, during, or after saturation). Examples are given in Table 10 for the highly exchanged products with platinum at high temperature (Experiment 1) and the mildly exchanged products with platinum or rhodium at ambient temperature (Experiments 2 and 12). In Experiment 1 half of the hydrogen liberated by exchange found its way into the gas phase where its final concentration was 0.9% (see Table 1). The other half was reused for saturation or further exchange. In Experiments 2 and 12 very little hydrogen was lost to the gas phase. The apparent surface concentrations of hydrogen in all three experiments were similar—about 3% in 1, 3.6% in 2, and 3% in 12. The computed yields of tetralin-$(h,d)_4$ were high, 91% to 92%, in Experiments 2 and 12, consistent with an associative mechanism for the adsorptions that lead to saturation. The reuse of hydrogen that had been liberated by exchange and retained on the catalyst necessarily shows up in the deuterium-deficient species. Tetralin-d_0, -d_1, and -d_2, were always present in larger than the computed concentrations, as if some of the hydrogen was being reused before it was completely mixed with the surface deuterium. Possibly, a molecule that is being dissociatively adsorbed is sometimes assisted by a neighboring molecule that is being associatively adsorbed in a concerted disproportionation reaction.

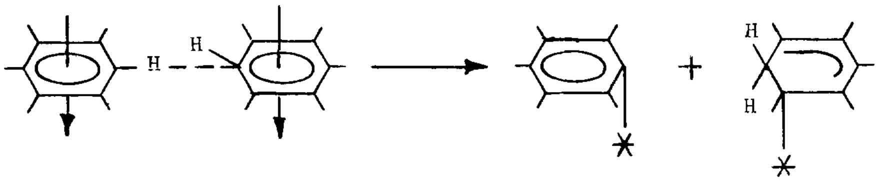


TABLE 10

CALCULATED $(h,d)_n$ VALUES AND D/H RATIOS FOR TETRALIN

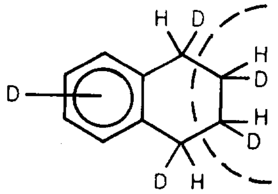
Experiment	n	Obs. d_n	Calculated	
			d_n	$(h,d)_n$
1	0	0.1	0.00	—
Pt, 200°	1	0.2	0.05	—
D/H = 32.3	2	0.6	0.26	—
	3	5.6	5.7	—
	4	47.6	47.6	49.72
	5	30.4	30.4	32.96
	6	11.6	11.6	13.14
	7	3.1	3.1	3.63
	8	0.7	0.7	0.86
	9	0.1	0.1	0.13
2	0	1.0	0.00	—
Pt, 25°	1	0.3	0.02	—
D/H = 26.8	2	1.3	0.65	—
	3	11.3	11.58	—
	4	77.9	77.9	90.70
	5	6.0	6.0	6.72
	6	1.35	1.35	1.62
	7	0.54	0.54	0.54
	8	0.25	0.25	0.42
12	0	0.14	0.00	—
Rh, 25°	1	0.11	0.11	—
D/H = 32.3	2	0.72	0.46	—
	3	10.9	10.87	—
	4	81.0	81.0	91.91
	5	5.6	5.6	6.30
	6	1.2	1.2	1.38
	7	0.26	0.26	0.28
	8	0.10	0.10	0.13

Other possibilities depend on heterogeneities in the surface, such as cracks or pores, where diffusion could be limiting.

The derived $(h,d)_n$'s for Experiment 1 showed that about half of the tetralin was tetralin-$(h,d)_4$, and the similarity of the distribution of isotopic species (Table 10) to those of the recovered naphthalene (Table 8) suggests that much of the extra deuterium in the tetralin was present before saturation. An estimate of the contributions of exchange (a) before saturation and (b) during or after saturation can be made by assuming that the contribution from the previously exchanged naphthalene is the average of its initial and final states.

Expt.	Distribution (%)		
	a	a + b	b
1	28	50	22
2	3.3	9.3	6.0
12	6.2	8.1	1.9

Presumably, the exchange that accompanies saturation will involve the ring that is being saturated. Exchange that follows saturation will be on the aromatic ring of tetralin.



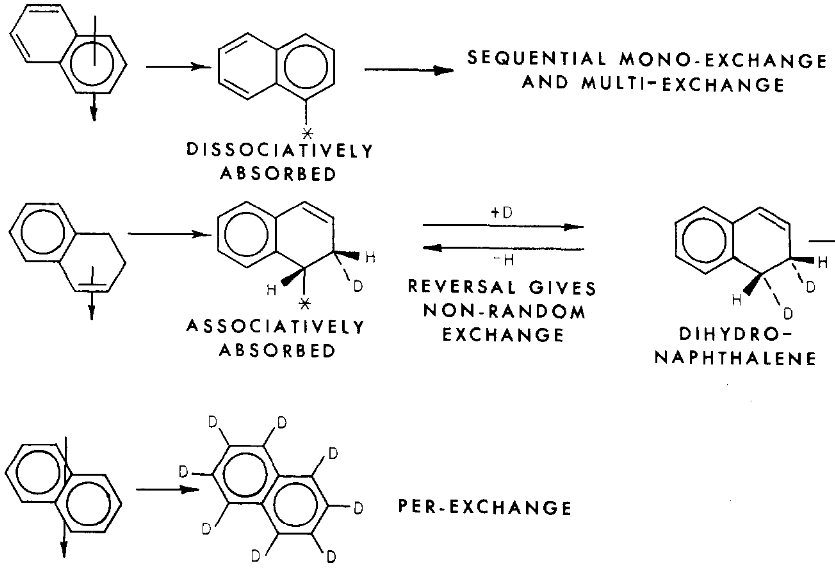
Deuterium distributions in the $C_8H_{8-n}D_n^+$ fragment ion are given in Table 2. The amount of deuterium lost with the ethylene fragment is expressed in Table 2 as a percentage of the total deuterium in the tetralin. The loss could range from a high of 50% for pure 1,2,3,4-tetradeuteronaphthalene (tetralin-d_4) to a low of 33.3% for completely equilibrated tetralin-d_4.

The two low-pressure runs (Experiment 4 with platinum and Experiment 11 with palladium) gave the lowest values—33% and 35%, respectively, showing that the slow rate of deuterogenation was accompanied by drastic redistribution, even to the extent of transferring aromaticity from one ring to the other.

In the high-pressure experiments the amount of deuterium lost with the ethylene fragment ranged up to 48%, but most of the results fell in the very narrow range of 44% to 45%. Assuming random distribution of the exchange that precedes saturation, the deviation from 50% means that subsequent exchange processes must have put excess deuterium either in the 1,4-positions (exchange during saturation) or in the aromatic ring (exchange after saturation). Examination of the tetralin, from Experiments 9 (palladium at 38°) and 14 (ruthenium at 25°), by nuclear magnetic resonance at 52 megacycles revealed that paladium did, indeed, put excess deuterium in the 1,4-positions whereas ruthenium put it mainly in the aromatic ring. The low values, 43% in Experiment 3 (platinum at 200°) and 41% in Experiment 8 (iridium at 200°), very likely reflect extensive exchange on the benzene ring in view of the massive exchange (70+%) on the recovered naphthalene.

Mechanisms of Naphthalene Reactions

A popular approach to mechanisms, and perhaps a good way to summarize for naphthalene, is to postulate the initial formation of a pi complex (*21–25*) of the reactant with the *d* orbitals of the metal such that the plane of the molecule will be parallel with the catalyst surface. Such a pi complex might involve any of the resonance forms of the naphthalene molecule. For present purposes we are not concerned with whether such a complex involves 1, 2, 4, 6, or 10 atoms of metal but intend only to suggest that what happens later may in some way be affected by the initial adsorption step.



Octalins in the Reaction Scheme

From work with xylenes on platinum catalyst, Siegel (*26*) proposed that cyclohexene isomers, although not detected, might serve as intermediates for the formation of *trans* isomers by *cis* addition of hydrogen. The extent to which each olefin isomer might participate depended on its chances of being formed by random addition of hydrogen around the ring. We found, with ruthenium catalyst, that the initial product from tetralin did indeed contain the statistical 2/1 ratio of $\Delta^{1,9}$- to $\Delta^{9,10}$-octalin in support of Siegel's hypothesis. The ratio changes rapidly as hydrogenation proceeds because the more exposed double bond of $\Delta^{1,9}$-octalin is saturated much more easily than the buried double bond in $\Delta^{9,10}$-octalin, especially on metals other than ruthenium. *cis*-$\Delta^{1,2}$-Octalin and *cis*-$\Delta^{2,3}$-octalin should be even more vulnerable to saturation. Although the trend was evident, we were not able to determine by actual measurement that *cis*-$\Delta^{1,2}$-octalin and *cis*-$\Delta^{2,3}$-octalin were formed in 2/1 ratio or that the amounts were as large as those of $\Delta^{1,9}$-octalin and $\Delta^{9,10}$-octalin, respectively. On the assumption that octalins are involved in statistical proportions and that those octalins in which the bridgehead hydrogens were already *cis* would yield only *cis*-decalin, we can make a rough estimate of the overall participation of octalins as intermediates.

Yields of *trans*-decalin from the saturation of $\Delta^{1,9}$-octalin and $\Delta^{9,10}$-octalin (see Table 3) and tetralin are recorded in Table 11. Without, at this point, justifying the mechanism whereby $\Delta^{9,10}$-octalin yields *trans*-decalin by the *cis* addition of hydrogen, we can use these data in a simple algebraic calculation.

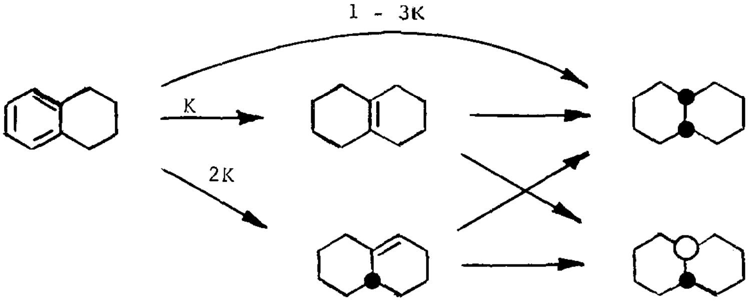
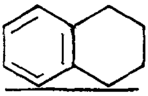
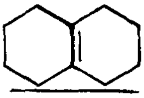
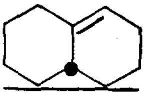


TABLE 11

Yields of *trans*-Decalin from Saturation of Tetralin and Octalins

	%-*trans*-Decalin		
			
Ru	5.5	5	26
Rh	11	15	41
Pd	53	85	82
Pt	16	38	62
Ir	7.5	2	26

For example, with ruthenium catalyst the yields of *cis*-decalin were 94.5% from tetralin, 95% from $\Delta^{1,9}$-octalin, and 74% from $\Delta^{9,10}$-octalin. Thus, we have the following results:

$$1.0(1-3K)+0.95K+0.74(2K)=0.945$$

$$0.57K=0.055$$

$$K=0.097$$

	% of Saturation via Octalin			
Catalyst	$\Delta^{1,9}$-	$\Delta^{9,10}$-	*cis*-$\Delta^{1,2}$-	*cis*-$\Delta^{2,3}$-
Ru	19.3	9.7	19.3	9.7
Rh	16.6	8.3	16.6	8.3
Pd	41.0	20.5	41.0	20.5
Pt	20.4	10.2	20.4	10.2
Ir	12.0	6.0	12.0	6.0

On this basis the overall participation of octalins is 40–60%, although for palladium it reaches the untenably high value of 123%. However, palladium was unusual in that the same high yield of *trans*-decalin was obtained from $\Delta^{9,10}$-octalin (~85%) as from $\Delta^{1,9}$-octalin. Very probably palladium isomerizes all octalin isomers to $\Delta^{1,9}$-octalin, which it saturates very rapidly. If so, the overall participation of octalins on palladium could be as low as 41%, and the direct saturation of the aromatic ring of tetralin to *cis*-decalin *a la* Balandin (*6*) would account for the other 60–40% of the mechanism on all of the metals.

Exchange on Recovered Octalins

Exchange was slow compared with saturation. In all experiments enough olefin was recovered for isotopic analysis (see Tables 4, 5, 6, 7), although in one case ($\Delta^{1,9}$-octalin on platinum) saturation was nearly complete. Considering the large amounts of exchange in the decalins, the unreacted octalins were remarkably little exchanged, except for $\Delta^{1,9}$-octalin on palladium (Experiment 20) and $\Delta^{9,10}$-octalin on rhodium (Experiment 27). The exchange pattern was very different from that for naphthalene at high temperature, where a mono-exchange process seemed to predominate, but rather similar to that for naphthalene at ambient temperature, where a multi-exchange mechanism seemed to be taking over. In a general way, the maximum number of positions exchanged seem to correlate with the number of allylic hydrogens—eight in $\Delta^{9,10}$-octalin and only five in $\Delta^{1,9}$-octalin. Unfortunately, the actual positions of exchange are not known and other interpretations are possible.

Isotopic Distributions in Decalins

Isotopic analyses for recovered octalin, isomerized octalin, *cis*-decalin and *trans*-decalin from the ambient-temperature deuterogenations on various metals are in Tables 4 and 5. Similar data on the 100° and 200° deuterogenations over platinum are in Tables 6 and 7. Considerable exchange always accompanied addition; none occurred after saturation. The yields of exchanged species are enhanced at high temperature because the adsorption of deuterium is reduced, and at low pressures because the saturation reaction is slowed. Thus, at 500 psig, $\Delta^{1,9}$-octalin gave a higher yield of dideuterodecalins at 100° (Experiment 15) but a lower yield at 200° (Experiment 16) than Smith and Burwell (*4*) obtained at 20° and atmospheric pressure.

The isotopic analyses from Tables 4 and 5 for the ambient-temperature deuterogenations over various metals are shown graphically in Fig. 1. The plots show rather strikingly the extent of differences among the metals. For example, with $\Delta^{1,9}$-octalin, platinum is outstanding for saturating the double bond with minimum exchange. Platinum and especially palladium favor formation of *trans*-decalin (Table 9), while ruthenium, rhodium, and iridium favor *cis*-decalin.

From $\Delta^{9,10}$-octalin one should have expected only *cis*-decalin, but palladium gave a very high yield of *trans*-decalin. The remaining metals favor *cis*-decalin but show a range of other selectivity differences. Platinum saturates $\Delta^{9,10}$-octalin with minimum exchange but, like ruthenium, shows very different isotopic distribution patterns in the *cis* and *trans* isomers, and gives *trans*-decalin the higher D average. The isotopic species of maximum yield is decalin-d_2 for ruthenium, *cis*-decalin-d_2 and *trans*-decalin-d_3 for platinum, decalin-d_3 for iridium and palladium, *trans*-decalin-d_3 and *cis*-decalin-d_4 for rhodium. Furthermore, *cis*-decalin from rhodium shows definite discontinuities in the exchange pattern following d_6 and d_{10}. These features will be discussed in more detail.

Computation of D/H Ratios and $(h,d)_n$'s for cis- and trans-Decalins

The same procedure was used as for tetralin except that a program in 12 binomials was written for the IBM 704. The observed and computed d_n's and computed $(h,d)_n$'s are given in Table 12 for platinum, Table 13 for ruthenium, Table 14 for iridium, Table 15 for palladium, and Table 16 for rhodium. For purposes of computation, the observed d_n's were arbitrarily ex-

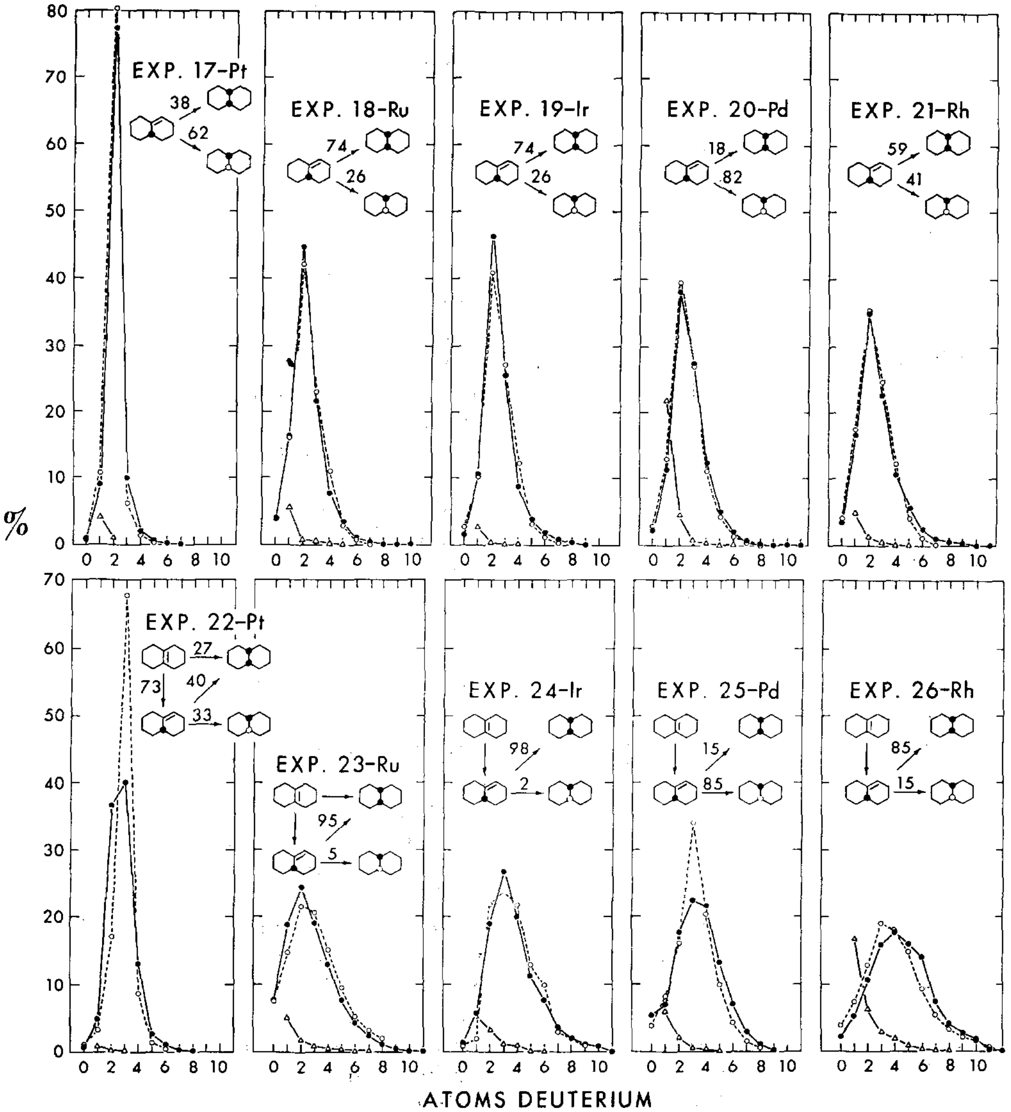


Fig. 1. Isotopic distributions in *cis*-decalin, *trans*-decalin, and recovered olefin from deuterogenation of $\Delta^{1,9}$-octalin (top) and $\Delta^{9,10}$-octalin (bottom) over platinum, ruthenium, iridium, palladium, and rhodium catalysts; ●, *cis*-decalin, ○, *trans*-decalin, △, octalin.

tended to d_{12} on the basis that yields below the level of detection would diminish in constant ratios.

In general, more positions in the *cis*-decalin were measurably exchanged than in the *trans*-decalin. For products from $\Delta^{9,10}$-octalin the programmed computation failed, even with 12 binomials, when the D/H ratios were low and the yields of highly exchanged species were appreciable. Platinum gave no trouble; palladium was borderline but a solution was obtained for *trans*-decalin from $\Delta^{9,10}$-octalin by adding two more binomials (Table 15).

Interpretation of Isotopic Distributions

The high yields of *cis*-decalin-$(h,d)_2$ and *trans*-decalin-$(h,d)_2$ on platinum (Table 12) show that $\Delta^{1,9}$-octalin is saturated by addition of two H,D atoms to one or the

TABLE 12

Derived D/H Ratios and $(h,d)_n$ Values for Platinum Catalyst

	Feed: $\Delta^{1,9}$-octalin (Expt. 17)						Feed: $\Delta^{9,10}$-octalin (Expt. 23)					
	cis-Decalin			*trans*-Decalin			*cis*-Decalin			*trans*-Decalin		
		Calc. for D/H = 17			Calc. for D/H = 15			Calc. for D/H = 14			Calc. for D/H = 12	
n	Obs.d_n	d_n	$(h,d)_n$	Obs.d_n	d_n	$(h,d)_n$	Obs.d_n	d_n	$(h,d)_n$	Obs.d_n	d_n	$(h,d)_n$
0	0.8	0.26	—	1.0	0.35	—	0.8	0.16	—	1.1	0.04	—
1	9.0	9.00	—	10.8	10.63	—	4.9	4.65	—	3.3	1.46	—
2	77.4	77.4	85.47	80.4	80.4	90.91	36.7	36.7	33.81	17.1	17.1	0.56
3	9.9	9.9	11.21	6.2	6.2	7.12	40.1	40.1	44.88	67.9	67.9	85.65
4	2.0	2.0	2.32	1.3	1.3	1.58	13.1	13.1	16.10	8.7	8.7	11.23
5	0.6	0.55	0.64	0.3	0.24	0.30	2.7	2.7	3.18	1.4	1.4	1.81
6	0.2	0.2	0.26	—	0.06	0.08	1.1	1.1	1.49	0.5	0.4	0.56
7	0.1	0.05	0.06	—	0.01	0.01	0.3	0.25	0.32	—	0.10	0.15
8	—	0.02	0.03	—	0.002	—	0.1	0.10	0.13	—	0.02	0.03
9	—	0.005	0.01	—	0.0004	—	0.1	0.04	0.06	—	0.004	0.01
10	—	0.0015	—	—	0.00007	—	0.1	0.015	0.02	—	0.0008	—
11	—	0.0005	—	—	0.000015	—	—	0.005	0.01	—	0.0002	—
12	—	0.0001	—	—	0.000003	—	—	0.002	—	—	0.00004	—

TABLE 13

DERIVED D/H RATIOS AND $(h,d)_n$ VALUES FOR RUTHENIUM CATALYST

	Feed: $\Delta^{1,9}$-octalin (Expt. 18)						Feed: $\Delta^{9,10}$-octalin (Expt. 24)	
	cis-Decalin			*trans*-Decalin				
		Calc. for D/H = 5.0			Calc. for D/H = 4.5			
n	Obs. d_n	d_n	$(h,d)_n$	Obs. d_n	d_n	$(h,d)_n$	*cis*-Decalin Obs. d_n	*trans*-Decalin Obs. d_n
0	4.1	1.48	—	3.9	1.65	—	7.7	7.6
1	16.3	15.53	—	16.1	15.78	—	18.9	14.8
2	44.8	44.80	51.39	42.2	42.20	46.99	24.5	21.6
3	21.8	21.80	29.00	23.1	23.10	26.67	19.2	20.7
4	7.8	7.80	10.12	11.0	11.00	18.44	13.1	15.2
5	3.4	3.40	6.33	2.9	2.90	5.60	7.8	9.6
6	1.0	1.00	1.45	0.7	0.70	1.93	4.4	5.3
7	0.5	0.50	0.92	0.1	0.10	0.25	2.4	3.2
8	0.1	0.20	0.50	—	0.03	0.08	1.2	2.0
9	0.1	0.07	0.14	—	0.01	0.03	0.5	—
10	0.1	0.03	0.10	—	0.003	0.01	0.2	—
11	—	0.01	0.02	—	0.001	—	0.1	—
12	—	0.003	0.03	—	0.0003	—	—	—

other face. Because the unreacted olefin was only mildly exchanged, except on palladium, we know that saturation is accompanied by much exchange but preceded by little.

The saturation of $\Delta^{9,10}$-octalin is different. In agreement with Smith and Burwell, (*4*) we found that all of the *trans*-decalin (on platinum and palladium) and some of the *cis*-decalin (on platinum) had reacted in at least three positions. Some of the *cis*-decalin had reacted in only two positions, definitely on platinum, probably on palladium and ruthenium, but no conclusion was possible on iridium and rhodium. The absence of *trans*-decalin-$(h,d)_2$ eliminates direct *trans* addition (*8*) as an operative mechanism on platinum and palladium in this system. A more likely mechanism is that some (~73% on Pt) of the $\Delta^{9,10}$-octalin was isomerized to $\Delta^{1,9}$-octalin, thereby gaining an atom of deuterium. De-

TABLE 14

DERIVED D/H RATIOS AND $(h,d)_n$ VALUES FOR IRIDIUM CATALYST

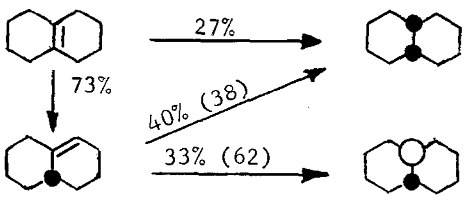
	Feed: $\Delta^{1,9}$-octalin (Expt. 19)						Feed: $\Delta^{9,10}$-octalin (Expt. 25)	
	cis-Decalin			*trans*-Decalin				
		Calc. for D/H = 8.5			Calc. for D/H = 7.0			
n	Obs. d_n	d_n	$(h,d)_n$	Obs. d_n	d_n	$(h,d)_n$	*cis*-Decalin Obs. d_n	*trans*-Decalin Obs. d_n
0	1.6	0.56	—	2.7	0.70	—	1.4	1
1	10.3	9.93	—	10.7	10.25	—	5.8	2
2	46.5	46.50	49.56	41.2	41.20	42.98	19.1	22
3	25.7	25.70	30.52	27.3	27.30	30.29	26.8	24
4	8.8	8.80	10.94	13.3	13.30	19.31	20.1	22
5	3.9	3.90	4.69	3.2	3.20	4.66	11.4	13
6	1.9	1.90	2.53	1.2	1.10	1.80	7.7	10
7	0.9	0.90	1.24	0.4	0.35	0.61	3.7	3
8	0.4	0.40	0.75	—	0.12	0.23	2.0	2
9	0.1	0.10	0.20	—	0.04	0.08	1.1	1
10	—	0.02	0.06	—	0.013	0.03	0.8	—
11	—	0.005	0.01	—	0.004	0.01	0.1	—
12	—	0.001	—	—	0.001	—	—	—

TABLE 15

DERIVED D/H RATIOS AND $(h,d)_n$ VALUES FOR PALLADIUM CATALYST

	Feed: $\Delta^{1,9}$-octalin (Expt. 20)						Feed: $\Delta^{9,10}$-octalin (Expt. 26)			
	cis-Decalin			*trans*-Decalin				*trans*-Decalin		
		Calc. for D/H = 6.0			Calc. for D/H = 5.5		*cis*-Decalin		Calc. for D/H = 4.8	
n	Obs.d_n	d_n	$(h,d)_n$	Obs.d_n	d_n	$(h,d)_n$	Obs.d_n	Obs.d_n	d_n	$(h,d)_n$
0	2.2	0.90	—	2.8	1.02	—	5.5	4.0	0.32	—
1	11.3	10.66	—	12.9	11.97	—	7.2	8.3	3.35	—
2	38.2	38.20	38.17	39.6	39.60	40.24	17.8	16.2	17.49	0.0
3	27.4	27.40	32.35	27.0	27.00	33.22	22.6	34.2	32.20	45.92
4	12.4	12.40	16.56	11.2	11.20	15.40	21.8	20.5	20.5	26.40
5	5.1	5.10	7.32	4.3	4.30	7.05	13.4	10.1	10.1	13.98
6	2.0	2.00	3.77	1.4	1.40	2.51	7.2	4.4	4.4	8.24
7	0.6	0.60	0.84	0.7	0.50	0.86	3.0	1.6	1.6	3.37
8	0.3	0.30	0.62	0.1	0.20	0.48	1.2	0.7	0.6	1.28
9	0.1	0.10	0.25	—	0.06	0.15	0.3	—	0.24	0.64
10	0.2	0.03	0.08	—	0.02	0.06	—	—	0.09	0.09
11	0.1	0.01	0.02	—	0.007	0.02	—	—	0.035	0.05
12	0.1	0.003	0.02	—	0.002	0.01	—	—	0.015	0.02
13								—	0.005	0.01
14								—	0.001	—

sorption need not be complete, but only sufficient for some molecules to flip over and readsorb on the other side.



The apparent failure of some molecules to desorb completely enough for flip-over is shown by a considerable favoring of *cis*-decalin beyond what would have been obtained (shown in parentheses on the road map) by adding $\Delta^{1,9}$-octalin to the liquid phase. This is a good example of a diffusion effect.

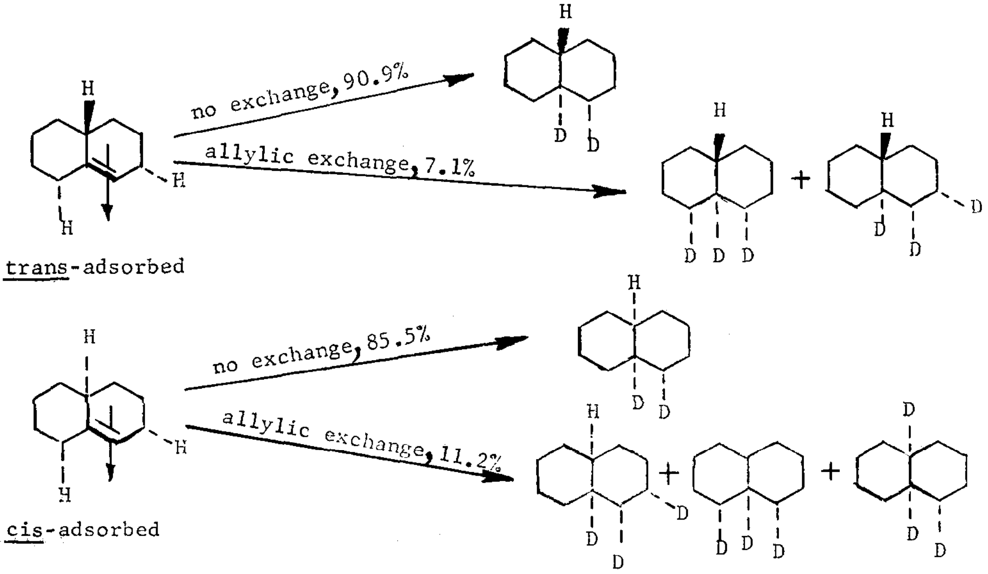
A special vulnerability to exchange in

TABLE 16

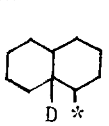
DERIVED D/H RATIOS AND $(h,d)_n$ VALUES FOR RHODIUM CATALYST

	Feed: $\Delta^{1,9}$-octalin (Expt. 21)						Feed: $\Delta^{9,10}$-octalin (Expt. 27)	
	cis-Decalin			*trans*-Decalin				
		Calc. for D/H = 3.5			Calc. for D/H = 3.0			
n	Obs.d_n	d_n	$(h,d)_n$	Obs.d_n	d_n	$(h,d)_n$	*cis*-Decalin Obs.d_n	*trans*-Decalin Obs.d_n
0	3.5	1.98	—	4.2	2.49	—	2.3	4.0
1	16.8	15.35	—	17.6	16.95	—	5.4	7.6
2	35.3	35.30	35.44	35.5	35.50	33.42	10.8	13.0
3	23.0	23.00	30.95	24.9	24.90	29.51	16.1	19.2
4	10.7	10.70	13.24	12.2	12.20	22.05	17.9	18.1
5	5.8	5.80	9.39	4.1	4.10	9.62	16.1	15.0
6	2.5	2.50	6.38	1.2	1.10	4.22	14.2	9.4
7	1.1	1.10	1.57	0.2	0.20	0.84	7.6	5.6
8	0.6	0.80	0.37	—	0.05	0.21	4.2	3.4
9	0.5	0.40	1.76	—	0.015	0.07	2.9	2.2
10	0.1	0.10	0.72	—	0.004	0.04	2.0	1.7
11	0.1	0.02	0.10	—	0.001	0.01	0.4	0.7
12	—	0.004	0.08	—	0.0003	0.01	0.1	0.1

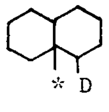
cis-adsorbed $\Delta^{1,9}$-octalin, presumably at position 10, was revealed on the platinum catalyst, by a difference between the yields of *cis*-decalin-$(h,d)_3$ (11.2%) and *trans*-decalin-$(h,d)_3$ (7.1%). The hydrogen at position 10 is an allylic hydrogen. Allylic C–H bonds are weaker by some 15 kcal than C–H bonds in the equivalent decalin. (*4*) $\Delta^{1,9}$-Octalin has five allylic hydrogens —two are exposed to the catalyst when *trans*-adsorbed and three when *cis*-adsorbed.



We propose that exchange occurs by dissociative adsorption at the allylic positions, one or more being exchanged during a single period of residence on the catalyst. Saturation proceeds independently of exchange by an associative mechanism, consistent with the increase in dideuterodecalins at high pressure. We have no evidence for a choice between 1-monoadsorbed-9-*d*-decalin,



and 9-monoadsorbed-1-*d*-decalin,



for the configuration of the half-hydrogenated intermediate from $\Delta^{1,9}$-octalin.

The exchange mechanism operative during the saturation of $\Delta^{1,9}$-octalin has a small tendency to exchange hydrogens in pairs rather than singly. The trends tabulated below become evident if K_i's are compared, as was done for naphthalene in Table 9.

The shift from odd numbers when the bridgehead hydrogen at position 10 is toward the catalyst to even numbers when it is away from the catalyst seems reasonable, but the reversal with palladium is strange. In *cis*-adsorbed $\Delta^{1,9}$-octalin the three allylic hydrogens at positions 2, 8, and 10 seem about equally vulnerable. By merely rolling on edge with the adsorbed double bond as a hinge, the second pair of allylic hydrogens at positions 2 and 8 would be accessible. Similarly, the *trans*-

Catalyst	Preferred number of exchanges during saturation of $\Delta^{1,9}$-octalin: *cis*-Decalin	Preferred number of exchanges during saturation of $\Delta^{1,9}$-octalin: *trans*-Decalin
Ru	1,3,5	2,4
Rh	1,3,7	2,4
Pt	1,3	2,4
Ir	1,6	2,4
Pd	2,4,6	1,3,5

adsorbed $\Delta^{1,9}$-octalin could expose two or four allylic hydrogens to the catalyst.

The decalins from $\Delta^{9,10}$-octalin fail to show any pattern of preference for particular numbers of exchanges. In all cases, the D averages are higher than for decalins from $\Delta^{1,9}$-octalin. Rhodium is especially active for exchange. The highest observed D averages were 4.51 for *cis*-decalin and 4.07 for *trans*-decalin, and the pattern for *cis*-decalin showed definite discontinuities following d_6 and d_{10}, corresponding to a preference for four and eight exchanges. A likely possibility is that the four allylic hydrogens on one side are exchanged, not necessarily all in a single residence period on the catalyst. Desorption and readsorption on the other side would expose the other group of four allylic hydrogens. An alternative that cannot be dismissed easily is that exchange propagates around one ring, replacing four hydrogens, and then around the other ring replacing four more. Such a mechanism, if the transition state leading to *trans*-decalin resembles *trans*-adsorbed $\Delta^{1,9}$-octalin, could account for a dearth if more highly exchanged species in *trans*-decalin by the difficulty of propagating exchange past the bridgehead when the hydrogen at position 10 is oriented away from the surface. Likely, both mechanisms are operative, but with the weaker allylic bonds getting preference.

Isomerization of Octalins

Even though $\Delta^{1,9}$-octalin is a prime intermediate in the hydrogenation of $\Delta^{9,10}$-octalin, its presence during the reaction would not be easily detected. It is both thermodynamically unfavored (12 to 1) and preferentially hydrogenated. A mere trace was detected in Experiment 26 and then perhaps only because palladium is such a good catalyst for double-bond isomerization relative to saturation.

$\Delta^{9,10}$-Octalin, if formed from $\Delta^{1,9}$-octalin by isomerization, should be easy to detect, but at ambient temperature none was found by Smith and Burwell (*4*). At higher temperatures enough is formed for detection. With platinum at 100° (Experiment 15) the concentration of $\Delta^{9,10}$-octalin was 2.6% at 47% saturation. With platinum at 200° (Experiment 16) its concentration was 4.4% at 95.5% saturation, and would likely have been higher had the reaction been stopped sooner. The isotopic composition of the isomerized octalin resembles that of its sister decalins so strongly as to suggest a common origin. Isotopic distributions in the $\Delta^{9,10}$-octalin recovered from ambient temperature deuterogenations with rhodium (Experiment 20) show very similar trends. Comparison can be made on the basis that saturation necessarily introduces two deuteriums while isomerization necessarily introduces only one. Thus, in Table 17 decalin-d_3 should be compared with $\Delta^{9,10}$-octalin-d_2.

TABLE 17
COMPARISON OF EXCHANGE PATTERNS
(EXPERIMENT 16)

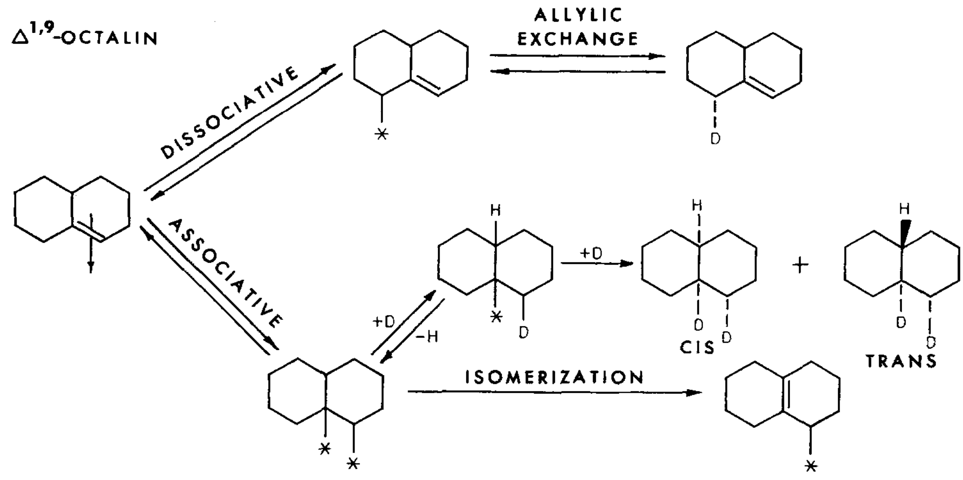
n	$\Delta^{9,10}$-octalin-d_n %	Decalin-d_{n+1} *cis* %	Decalin-d_{n+1} *trans* %
2	24.2	24.2	23.1
3	12.8	12.0	12.4
4	8.2	7.2	6.3
5	4.6	4.1	3.2
6	2.3	2.5	1.7
7	1.4	1.3	0.8
8	0.7	0.9	0.2
9	0.4	0.3	0.4

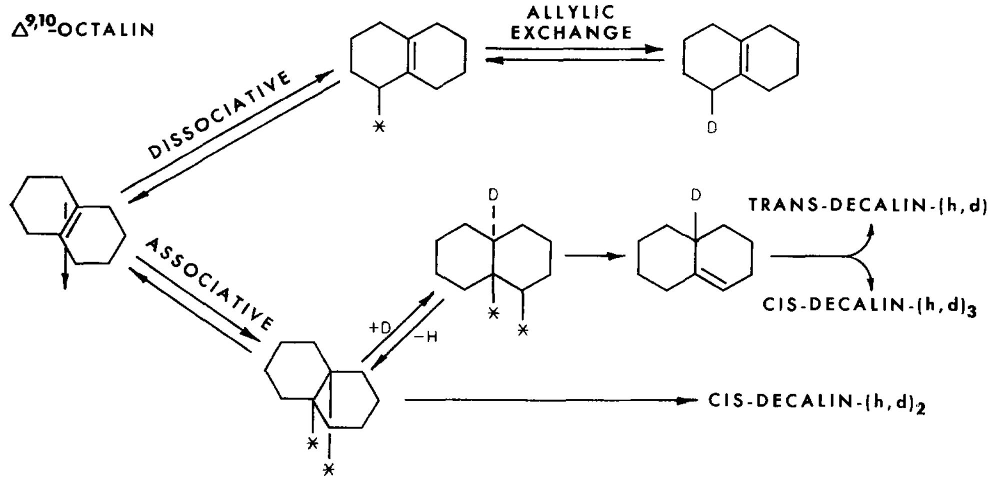
A likely common source for all three products is the 9-monoadsorbed species. The exchange could have occurred by the classical mechanism (*3*) of alternation between monoadsorbed and diadsorbed radicals.

Mechanisms of Octalin Reactions

That an associative mechanism operates for saturation is shown by the preponderance of *cis*- and *trans*-decalin-$(h,d)_2$ from $\Delta^{1,9}$-octalin and a significant yield of *cis*-decalin-$(h,d)_2$ from $\Delta^{9,10}$-octalin. The lack of *trans*-decalin-$(h,d)_2$ from $\Delta^{9,10}$-octalin rules out simple *trans* addition at the positions 9 and 10.

A dissociative mechanism for saturation of all or part of the $\Delta^{9,10}$-octalin is unattractive because of the presence of *cis*-decalin-$(h,d)_2$. Isomerization by an associative mechanism to $\Delta^{1,9}$-octalin could





account for all of the *trans*-decalin and part of the *cis*-decalin having reacted in at least three positions—one for isomerization and two for saturation. Furthermore, the identical exchange patterns of the $\Delta^{9,10}$-octalin from isomerization of $\Delta^{1,9}$-octalin with the decalins from saturation point to a common intermediate that resembles the "half-hydrogenated state" as pictured in an associative mechanism.

A dissociative mechanism is favored for the exchange that precedes saturation both for naphthalene and for the octalins. It is consistent with the predominantly mono-exchange, repeated-adsorption pattern for naphthalene at high temperature and the shift toward multi-exchange per residence at lower temperature. The similarities in the exchange patterns of naphthalene and the octalins suggest similar mechanisms. The preservation of the double bond of $\Delta^{1,9}$-octalin in a vulnerable position during exchange argues against disruption of the pi-electron system by associative adsorption. In more subtle detail, the numbers of positions exchanged seem to follow the numbers of allylic hydrogens available. If part of the mechanism of exchange during saturation involves alternation between mono-adsorbed and α,β-di-adsorbed olefin, the adsorption complex seems to retain more memory of the original identities of the allylic and nonallylic hydrogens than would be expected.

The addition reaction, both for naphthalene and the octalins, is so facile that it scavenges hydrogens placed on the surface by exchange and keeps the concentration quite low. *trans*-Adsorbed $\Delta^{1,9}$-octalin seems to see a slightly lower D/H ratio than does *cis*-adsorbed $\Delta^{1,9}$-octalin. The mechanistic steps can be pictured as proceeding from an initial pi complex.

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